

Water Quality Assessment of the Los Angeles River Watershed, California, USA in Wet and Dry Weather Periods

Mohammad Hassan Rezaie Boroon^{1*} and Carl Brian Von L. Coo¹

¹Geosciences and Environment Department, California State University, Los Angeles, USA.

Authors' contributions

This work was carried out in collaboration between both authors. Author MHRB designed the study and wrote the first draft of the manuscript, managed the literature searches, and analyses of the study and data. Author CBVLC managed the experimental process, performed the ion chromatography analysis and wrote the protocols. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/JGEESI/2015/20717

Editor(s):

- (1) Yan Maochao, Institute of Geographic Science and Natural Resource Researches, Chinese Academy of Science, China.
- (2) Zeyuan Qiu, Department of Chemistry and Environmental Sciences, New Jersey Institute of Technology, USA.

Reviewers:

- (1) Anonymous, Hong Kong Polytechnic University, Hong Kong, China.
 - (2) Pavlina Simeonova, Institute of Solid State Physics, Bulgaria.
 - (3) Antonio José Gazonato Neto, Federal University of São Carlos, Brazil.
- Complete Peer review History: <http://sciencedomain.org/review-history/11479>

Original Research Article

Received 5th August 2015
Accepted 1st September 2015
Published 19th September 2015

ABSTRACT

River runoff in semi-arid urban watersheds may consist entirely of treated wastewater effluent (dry-weather) and/or urban nonpoint source runoff (wet-weather), which can be a source of nutrients, bacteria, and metals to receiving waters. The purpose of this study is to identify sources of potential pollutants and to characterize urban water quality along the Los Angeles (LA) River from its head to the mouth during dry and wet weather seasons. The LA River is an effluent-dominated water body during the dry season. The three wastewater treatment plants (WWTP) including the Tillman, Burbank, and Glendale waste water treatment plants discharge the majority of the volume flowing in the LA River during the dry and wet period. The WWTPs discharge chemicals such as chloride, nitrate, and sulfate to the river. The metals are more likely attributed to street runoff. In both cases, the contamination is dispersed through various water channels that carry semi treated effluent from various sources ending up into the ocean. To understand seasonal and spatial pattern of these

*Corresponding author: Email: mrezaie@exchange.calstatela.edu;

contaminants, the water samples for chemical and physical analysis were collected along the LA River to assess the recent pollutant deposition processes in response to extensive human activity in wet and dry seasons. The general trend of the results shows that the concentrations of anions are higher during the dry season in compare to the wet season. Anion concentration values (ppm) in the dry season ranging from 5.5-16,027 (chloride), 0-1.0 (fluoride), 0-21 (nitrate), 0-1.6 (phosphate), and 13.3-2,312 (sulfate); whereas the values (ppm) for anions in the wet season ranging from 3.4-5,860 (chloride), 0-0.66 (fluoride), 0-17 (nitrate), 0-0.67 (phosphate), 7.9- 745 (sulfate). Dry season concentrations values for trace metals were obtained with values (ppb) ranging from 0.9-10 (nickel), 0.8-62 (zinc), 1-4 (arsenic), 0-1 (lead) and 0-3 (selenium). As for the wet data for trace metals (ppb) ranging 0.001-0.008 (nickel), 0.000001-0.038 (zinc), 0.0016-0.016 (arsenic), 0.00099-0.0058 (lead), 0.000001-0.0093 (selenium). Data were used to calculate mean concentrations and loads for various sources. The most likely sources for chloride are the three WWTPs in the Sepulveda Basin, Burbank, and Glendale. Other source for higher chloride level may be the tidal effect in the region closer to the ocean. The source of nitrate loading is attributed to storm drains including lawn fertilizers, septic systems, WWTPs, and agricultural runoffs in headwater area. Comparison of wet vs. dry weather loading indicates that dry weather loading can be a significant source of metals. This study indicates that constituent loading during the dry weather period can comprise a substantial portion of the total annual load in LA River urban watersheds, such as those investigated in this study. Moreover, the risks posed by the metals were highest in the dry season due to dry season runoffs. In water-limited areas such as the Los Angeles basin, urban runoff is a water resource that could improve restricted water supplies and to enhance localized renewable groundwater resources. Thus, an assessment of this precious water resource is important for local cities and regulatory organizations.

Keywords: Nonpoint and point source pollution; pollutant load; urban watershed; urban water; urban runoff.

1. INTRODUCTION

In urbanized regions, persistent environmental pollutants (POPs) such as heavy metals and trace elements can cause serious damage to ecosystem's health [1]. These pollutants originate either from natural processes such as atmospheric deposition [2] and geological weathering [3,4] or from anthropogenic sources such as industrial wastewater and domestic sewage and waste water treatment plants [5,6]. The Los Angeles metropolitan region, through which the Los Angeles (LA) River flows, consists of residential, commercial, and industrial areas. According to the Los Angeles County Department of Public Health [7], the LA River watershed is composed of 44 cities and other unincorporated communities with an approximate population of 9 million people. Hence, land use distribution of the LA River watershed include 44% open space, 37% residential, 11% industrial, and 8% commercial [8].

The LA River is a fully engineered flood control system running through a complex urban watershed [9]. Furthermore, the LA River is one of the most highly modified water systems in the world [10]. This concrete-lined southward flowing river channel runs through Los Angeles, where

railroads, freeways, and major commercial and government buildings of the City border the channel. The cities in this urban watershed include City of Bell, Burbank, Glendale, Los Angeles, and Long Beach. Several industrial services discharge into the LA River, but the vast majority only discharge surface runoff during storm events [10]. Furthermore, the surface runoff from the LA River represents approximately 33% of the gauged runoff in the region [11]. Urban runoff contributes human waste and organic bacteria [12]; trace metals (chromium, copper, lead, and zinc) and nutrients (nitrate and phosphorus) to the channel before it discharges to the southern California coastal ocean. Other input sources include three wastewater treatment plants (WWTP), which use tertiary treatment for municipal and industrial wastewater. The Tillman and Glendale WWTP discharge their effluents directly to the LA River [13]. The Burbank WWTP discharges its effluents to the Burbank-Western Channel, a major tributary, which is just upstream of its confluence with the LA River. The groundwater seepage counts as additional natural discharge to the LA River.

As a result of flood control measures undertaken, dramatic modifications have successfully

reduced flooding and property damage, although little of the engineered design has incorporated water quality improvements [10]. In general, urbanization in arid and semi-arid regions, such as southern California, can impact stream and drinking water quality negatively by increasing the addition of organic pollutants, metals, and nutrients in surface and ground water [14-16]. Yet, little is known about how the characteristics of the stream channel substrate, wastewater treatment plant's runoff, and specifically, the storm water drainage system along the LA River, alter the hydrochemistry of urban river runoff. Consequently, segments of this water body are included in the list of impaired waters in California as stated in the State Water Resources Control Board's section 303 (d), Clean Water Act, 1972 [17].

Dry weather runoff in arid, urban watersheds may consist entirely of treated wastewater effluent and/or urban nonpoint source runoff, both of which can be a source of bacteria, nutrients, and metals to receiving waters [18]. Comparison of wet vs. dry weather loading indicates that dry weather loading can be a significant source of metals, ranging from less than 20% during wet years to greater than 50% during dry years [13]. In winter (wet season), flowing water in the LA River is mainly attributed to runoff from the streets of the heavily populated and urbanized area including the City of Los Angeles, City of Bell, and Long Beach. Little research has focused on dry estimate of heavy metal and trace elements loads to LA River during summer (dry season). This research study aims to assess the water quality of the LA River in both wet and dry seasons. Consequently, to achieve water quality objectives [19] we have conducted water sampling during the dry and wet periods in the river watershed to evaluate the seasonal and spatial changes of various physio-chemical parameters (pH, dissolved oxygen and temperature, anions and cations) and heavy metal concentrations (arsenic, selenium, lead, nickel, and zinc) distribution. Water samples from the main course of the river and its tributaries provide a good representation of water quality that is influenced by many different point and nonpoint sources of pollution affecting the river's hydrochemistry.

Overall, the goals of this study are a) to characterize the water quality in the LA River and the various loads to the watershed system, b) to gain a better understanding of the fate and transport of chemicals by speciation and

movement, and c) to link the water quality of the LA River with dry and wet urban runoffs. Furthermore, it is important to realize that in water limited areas such as the Los Angeles basin, urban runoff is a water resource. Thus, a specific goal is to provide future management action alternatives. Through active management recharge, we would be able to enhance limited water supplies and increase localized renewable groundwater resources.

2. METHODS

2.1 Study Area

The LA River watershed is one of the largest in the Southern California region covering about 2160 km² (834 mile²). To the north the LA River is bounded by the San Gabriel Mountains, and it flows approximately 82 km (51 miles) from the Santa Monica Mountains at the western end of the San Fernando Valley to the Pacific Ocean. The river consists of 94% concrete banks and about 75% hard concrete bottom. It is unlined in three places including Sepulveda Basin, Glendale Narrows, and near mouth of the river in the Long Beach area. The channel is over 152 m (500 feet) wide in some places. Two distinct characteristics represent the topography of the LA River watershed includes the very steep mountain regions and the low lying relatively flat sections in the San Fernando Valley as well as the lower LA River. The headwater of the river is at the convergence of Bell Creek and Calabasas Creek in the Canoga Park area of the San Fernando Valley (NW of Los Angeles). Bell Creek drains the Simi Hills and receives the discharge from Chatsworth Creek. From the confluence of Arroyo Calabasas and Bell Creek, the LA River flows east through the southern portion of the San Fernando Valley, a heavily developed residential and commercial area. Headwaters in the Santa Monica, Santa Susana and San Gabriel Mountains are covered by vegetation and open spaced covering approximately 943 km² (364 mile²); the remainder of the watershed is highly developed. Major tributaries to the river in the San Fernando Valley are the Pacoima Wash, Tujunga Wash (both drain portions of the Angeles National Forest in the San Gabriel Mountains), Burbank Western Channel, and the Verdugo Wash (both drain from the Verdugo Mountains) [20] (Fig. 1).

The LA River turns in an area known as the Glendale Narrows and flows south for

approximately 40 km (25 miles) through industrial and commercial areas and is bordered by rail yards, freeways, and major commercial and government buildings. Below the Glendale Narrows, three major tributaries feed the Los Angeles River-Arroyo Seco Wash, Rio Hondo, and Compton Creek. The river discharges to the Pacific Ocean at Queensway Bay, a portion of San Pedro Bay in Long Beach [20] (Fig. 1).

2.2 Water Quality Parameters

Water quality in a stream is the product of the quality of the precipitation and any changes that have occurred to the water at or below the surface of the earth. As water moves through

different locations, it changes chemically, physically, and biologically. Some constituents affect taste (chloride and sulfate), others may be corrosive (high in dissolved solids, low pH) and a few may be health hazard (heavy metals, nitrate). In order to meet water quality objectives, we have selected the parameter from National Primary Drinking Water Regulations [21]. The selected contaminant includes arsenic, lead, nitrate, selenium. Other inorganic chemicals often present in trace quantities are also important water quality factors and some have implications for human health. The selected parameters in the secondary maximum contaminant level include sulfate, fluoride, chloride, and zinc.

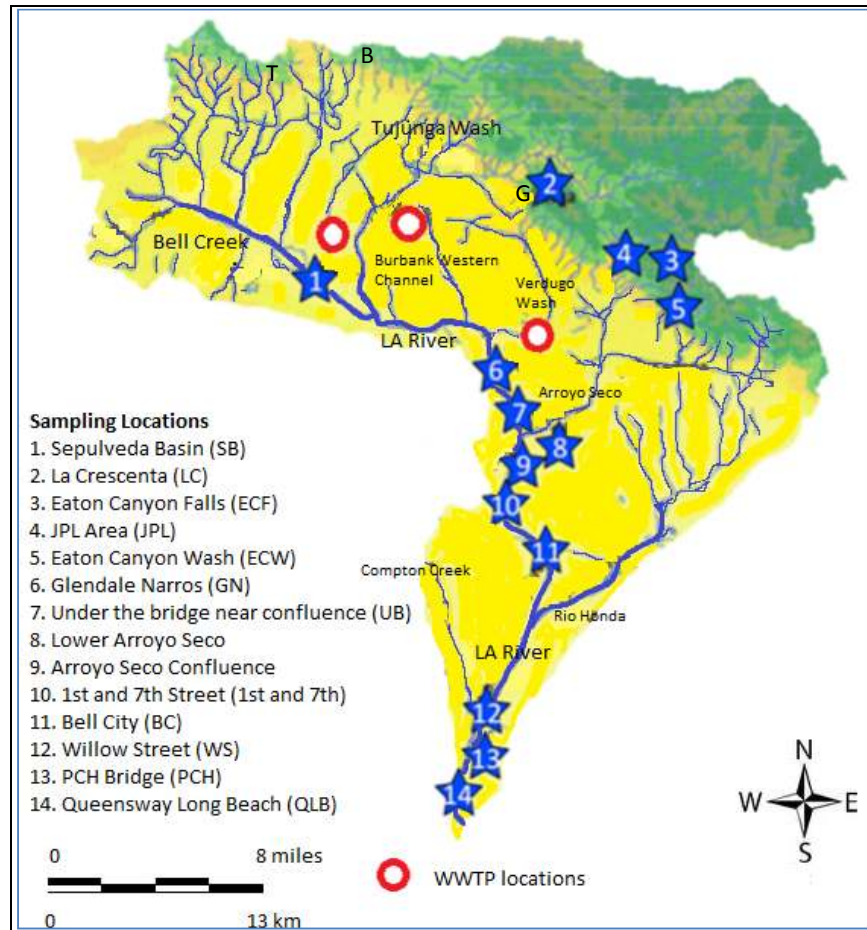


Fig. 1. Map of the LA river watershed and the approximate sampling locations (modified from [20]).

The 3 Waste Water Treatment Plants (WWTP) include the Tillman (in Van Nuys) and Glendale WWTP, which discharge their effluents directly to the LA River. The Burbank WWTP discharges to the Burbank-Western Channel, a major tributary, which is just upstream of its confluence with the LA River. Tillman WWTP (T); Glendale WWTP (G); Burbank WWTP (B)

2.3 Sampling Locations

Samples on the concrete-lined section of LA River were taken at various sites from the Sepulveda Basin to Long Beach. Fourteen (14) locations for water samples were designated along the river channels and at the recharge area in the northern portion of the basin. These locations including the Sepulveda Basin (1), La Crescenta (2), Eaton Canyon Falls (3), JPL Area (4), Eaton Canyon Wash (5), Glendale Narrows (6), Under the bridge near Confluence (7), Lower Arroyo Seco (8), Arroyo Seco Confluence (9), First and Seventh Street (10), Bell City (11), Willow Street in Long Beach (12), Pacific Coast Highway Bridge (13) and Queensway in Long Beach (14) (the mouth of the LA River). Water samples from sites with natural waters were also taken. These sites include La Crescenta, Eaton Canyon Wash, and JPL. Groundwater discharge is the main source of the headwater that feeds Los Angeles River, particularly in wet seasons (Fig. 1).

Two water samples were taken from each of the specified locations, one unpreserved and the other preserved with Nitric Acid (HNO_3 1 N). The samples were filtered with a $0.45 \mu\text{m}$ syringe filter before acid preservation. Samples were taken at the center of the stream where the river flow is highest and the water is homogeneous. During the wet season and in the high peak flow discharge condition, we obtained the water samples from the middle of the river using Niskin bottle sampler. This device is a large sampling bottle with spring loaded valves at both ends that are closed at appropriate depth by a messenger device sent down the wire connecting the bottle to the surface. The sampler was lowered often from a bridge over the center of the river to get a water sample. Each time that the Niskin bottle sampler was used it was rinsed by deionized water to prevent cross-contamination of the water samples. Sampling at all locations was done during the wet and dry period of the river. Wet sampling was done during February and March of 2011, and dry period sampling was done during the months of July and August of 2011. The physio-chemical parameters of the river water were analyzed at the sampling site and included pH, dissolved oxygen, temperature, and salinity. Temperature and pH were obtained using an Accumet AP71 probe on a 2-point calibration. Salinity (in parts per thousand $^0/_{00}$) was measured using a hydrometer; which uses water density to measure the corresponding salinity. Dissolved Oxygen was measured in the

field using a handheld dissolved oxygen instrument (YSI 550A). All instruments were calibrated prior to use in the field in order to attain accurate readings for the test performed. Anions, including fluoride, chloride, nitrate, phosphate, and sulfate, were analyzed using a Dionex ICS-1000 Ion Chromatography (IC) System at the hydrogeology laboratory at Cal State LA. The Ion Chromatography System runs on a $25 \mu\text{m}$ sample loop, $4 \times 250\text{mm}$ AS14A Column, and Sodium Carbonate/Sodium Bicarbonate eluant. Samples are stored at a temperature of 4 degrees Celsius and were filtered using a $0.45 \mu\text{m}$ syringe filter prior to analysis. According to EPA standards, all analysis for nitrate and phosphate were conducted within two days after sampling; and chloride, fluoride, and sulfate were analyzed no later than 28 days after the sampling event.

The IC system was set up on a 4-point linear calibration with at least 99.95% correlation coefficient. Analytes are separated by the column into different elution times depending on the eluant and column used; this would then eventually go to the detector to quantify each calibrated target compound. The elution time or retention time was the time specified for an anion's peak to appear. This is obtained from the certificate that comes with the IC system and the column certificate and the calibration was based from there. Calibration is necessary for every instrument used to assure that the data produced is accurate or precise. Calibration Verification (CV), known concentrations of the Dionex fluoride, chloride, nitrate, phosphate and sulfate standards, was analyzed at intervals of every 10 samples for quality control. All calibration verification on this set of samples was within 80-120% recovery. Samples from the dry and wet periods of the river were analyzed for metals including arsenic, lead, selenium, nickel and zinc. The wet period samples were analyzed by the Scripps Institute of Oceanography, excluding La Crescenta and Eaton Canyon waterfall due to lack of samples. The water samples were analyzed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) 3000 XL with detection limits ranging from 0.05×10^{-6} to $4.0 \times 10^{-6} \text{ mg g}^{-1}$ depending on the element (Perkin Elmer, CA, USA). QA and QC were assessed using duplicates, method blanks and standard reference materials according to EPA standard.

Analyzes for the dry period samples were done using Perkin Elmer ELAN 6100 ICP-MS

(Inductively Coupled Plasma-Mass Spectrometry) at California State University, Bakersfield. The samples were filtered using a 0.45 mm syringe filter and then preserved with nitric acid on the field. The ICP-MS is on a 3-point calibration with a calibration coefficient of 99.9% that is linear through zero and calibration verification within 80-120% recovery.

2.4 Quality Assurance (QA) of Analysis

To ensure the quality of the data produced calibration is very important for the instruments. Handheld instruments such as the pH and DO meter were calibrated each time they were used in the field. Most instruments used are automated and calibrations were computerized. Instruments like the Ion Chromatography System and the ICP-MS were calibrated before analysis or every three months depending on the specifications given by the manufacturer. Blank testing is an important analysis for the assurance of zero or minimal contamination on the system. The Ion Chromatograph uses linear calibration on the instrument, plotting the area under the curve of the chromatographs versus the known concentration of the standard. The computer calculates the concentration of samples using the linear equation from the graph. The calibration results for anions showed a correlation coefficient of at least 99.95% on each target anion. Calibration verification was shown on a table with 80% to 120% recovery of the known standard. ICP instruments use linear calibrations and, in this case, based on the mass intensity of the sample and the known concentration.

2.5 Statistical Analysis

Statistical analysis *t*-Test and Correlation were conducted for comparisons between the dry and wet season concentration values and for differentiating the relationship between concentration values during the dry season. The significance level was set at $\alpha = 0.05$ for all statistical tests and qualitative assessment using EXCEL. Field replicate and blank samples also were taken on site to ensure the quality of data.

3. RESULTS

3.1 Temperature, pH, Dissolved Oxygen (DO), and Salinity

As it was expected, the results showed higher water temperature for the LA River during the dry period. The dry period had a temperature range

from 16-26°C with an average of 20.6°C. During the wet periods, temperatures ranged from 9-18°C with an average of 14.9°C. (Table 1)

The pH measurements in the study area showed a pH range from 4.88 to 8.6 with an average pH of 7.27 for the dry period and 7.5 to 8.5 with an average of 7.96 during the wet period. It is evident that besides the Tillman treated water; the additional source to LA River water in the dry season is groundwater seepage with a slightly acidic pH value. For both periods, the pH is within the natural level, except for sample 13 (PCH Bridge) where the pH was 4.88. Here, a large quantity of solid waste and oil residue was observed, which may have contributed to the point source pollution at this site. The California Water Quality Control Board has also reported [22] that the discharge of water with pH levels above standard from some tributaries (such as Arroyo Seco) may have contributed to higher pH levels in LA River.

The concentrations of dissolved oxygen (DO) in the LA River watershed for the dry period ranged from 5.8 to 12.2 mg/L with an average concentration of 8.9 mg/L. During the wet period DO ranged from 6.9 to 17.9 mg/L with an average of 10.3 mg/L. DO values showed higher concentrations (positive trend) during the wet period as compared to the dry period. Sample 1 (Sepulveda Basin-unlined river bottom) showed the highest DO level and sample 14 (Queensway) showed the lowest concentration (Table 1). The higher pH value (slightly alkaline condition) in the unlined section of LA River may have been the result of a high rate of photosynthesis by attached algae on the river bed, as dissolved oxygen measurements for the site 11 and 12 for dry and wet monitoring periods peaked in same sites.

Overall, very low salinities were recorded for all stations except sample 13 (PCH Bridge) and sample 14 (Queensway). The higher salinity values occurred in sites closer to the ocean, where seawater and fresh river water mixed during high tide conditions (Table 1). Fig. 2F shows also the correlation of wet and dry weather conditions for this parameter.

3.2 Chloride, Fluoride, Nitrate, Phosphate, and Sulfate

During the dry period of the river, chloride concentrations ranged from 5.5 mg/L to 16,027 mg/L with an average of 1,589 mg/L. The high chloride concentrations were recorded near the

ocean (samples 13 and 14) and ranged from 5395 to 16,027 mg/L. The concentrations along unlined segments of the river were 5.5 to 108 mg/L (samples 1, 2, 3, 4, and 5), where groundwater seepage and industrial runoff occur. The chloride concentration was highest where the ocean experienced the high tide (river and ocean water were mixed) and the lowest concentration where the river water was mixed

with groundwater seepage. In addition, the concentration of chloride was higher during dry periods compared to the wet sampling period. During the wet period, concentrations of chloride ranged from 3.4 to 5,860 mg/L with an average concentration of 444 mg/L. High chloride concentration were determined from samples 1 and 14 with the concentration of 120 and 5860 mg/L (Table 2). Excess concentration of these

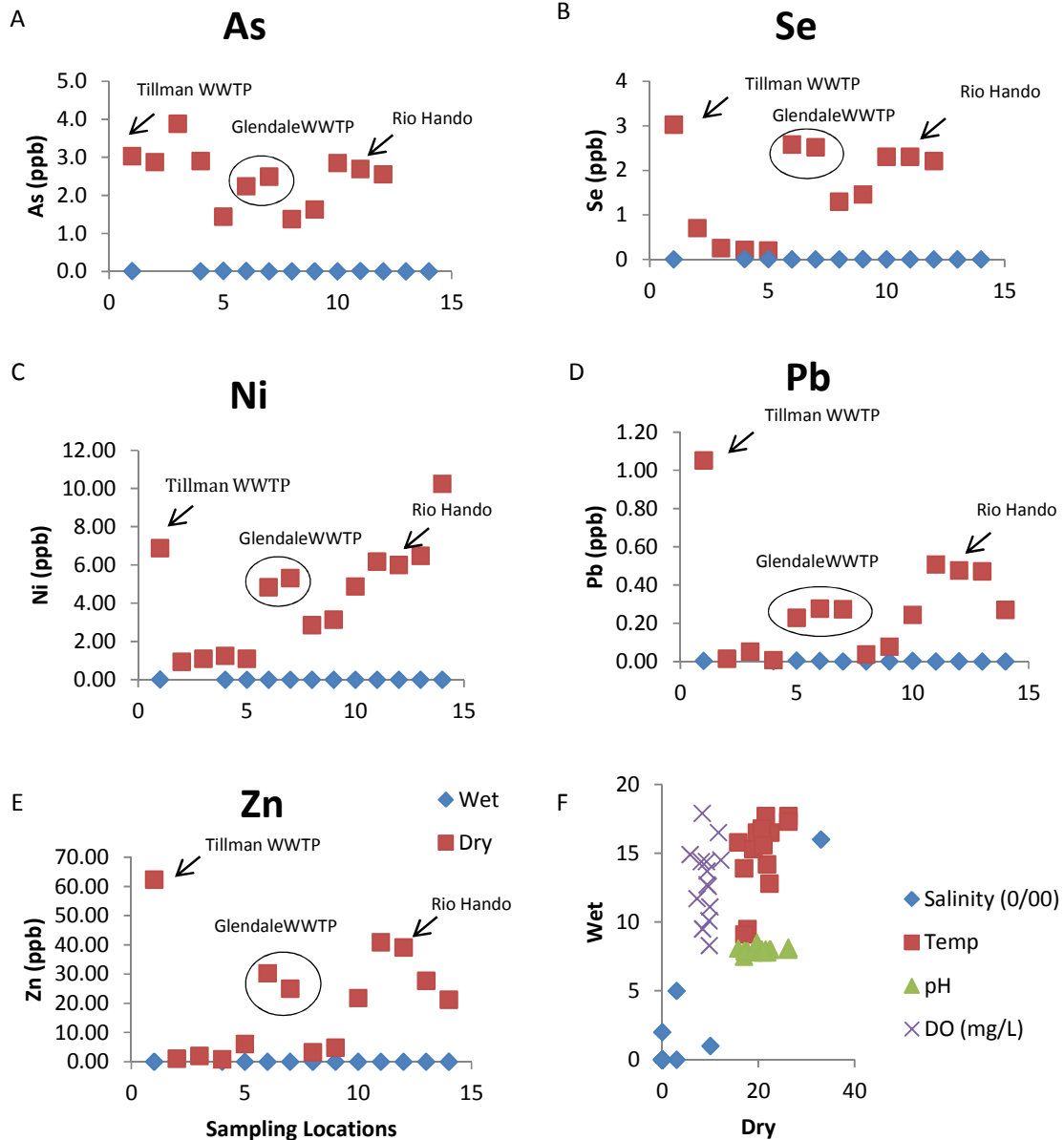


Fig. 2. (A-E) The metal concentrations (ppb) during the dry and wet period for Los Angeles River in various sampling sites. WWTP Waste Water Treatment Plant. (F) The scatter plot for the various physio-chemical parameter in the wet and dry period. N (dry)=14 and N (wet)=14

Table 1. Spatial and seasonal changes of various water parameters for LA river

Sampling Location	Dist km (mile)	Dry Season				Wet Season			
		DO (ppm)	pH	Temp (°C)	Salinity (‰)	DO (ppm)	pH	Temp (°C)	Salinity (‰)
1	71 (44.1)	8.3	7.94	26.2	3	17.9	8.14	17.7	5
2	63 (39.2)	9.8	8.08	15.8	0	8.3	8.08	15.8	0
3	58 (36.5)	9.7	7.6	17	0	10.1	7.5	13.9	0
4	58 (35.9)	9.6	7.29	17.7	0	12.6	7.9	9.5	0
5	56 (35.2)	9.3	7.29	17.1	0	12.7	7.9	9.1	0
6	47 (29.4)	7.24	6.8	21.8	0	11.7	7.8	14.2	0
7	40 (25.1)	8.1	6.27	22.3	0	14.4	8	12.8	0
8	40 (25.1)	9.9	6.98	18.9	0	11.1	7.8	15.3	0
9	40 (25.0)	9.3	7.15	19.7	0	13.7	8.5	16.5	2
10	35 (21.8)	9.2	7.03	22.5	0	14.4	8	16.5	0
11	26 (16.1)	11.7	7.94	26.2	3	16.5	8	17.3	0
12	6 (4.0)	12.2	8.63	21.5	0	14.5	8	17.7	0
13	5 (3.0)	8.4	4.88	20.7	10	9.5	8	16.8	1
14	1 (0.9)	5.8	7.97	21	33	14.9	7.8	15.6	16
Minimum		5.8	4.88	15.8	0	8.3	7.5	9.1	0
Maximum		12.2	8.63	26.2	33	17.9	8.5	17.7	16
STD. Dev.		1.63	0.92	3.18	8.92	2.70	0.22	2.77	4.33
Average		9.18	7.27	20.60	3.50	13.02	7.95	14.90	1.71

The table also shows a comparison of average, standard deviation (SD), minimum, and the maximum of various parameter in the various locations in LA River. Sampling location 1 and 14 were furthest and closest to the ocean. These locations including the Sepulveda Basin (1), La Crescenta (2), Eaton Canyon Falls (3), JPL Area (4), Eaton Canyon Wash (5), Glendale Narrows (6), Under the bridge near Confluence (7), Lower Arroyo Seco (8), Arroyo Seco Confluence (9), First and Seventh Street (10), City of Bell (11), Willow Street in Long Beach (12), Pacific Coast Highway Bridge (13) and Queensway in Long Beach (14) (The Mouth of the LA River). MCL=Maximum Contamination Limit, na = Not Available. N (dry)=14 and N (wet)=14

constituents can be harmful to human health. The US Environmental Protection Agency set the maximum contaminant levels (MCL) for chloride to be 250 ppm [23].

The fluoride concentrations ranged from 0 to 0.66 mg/L for the wet period and 0 to 1.032 mg/L for the dry period with an average concentration of 0.37 mg/L during the wet period and 0.56 mg/L during the dry period (Table 2). Excess concentration of these constituents can be harmful to human health. The US Environmental Protection Agency set fluoride MCL to be 4 ppm [23].

The results showed also a range of nitrate concentration during the dry period of 0 to 21.5 mg/L (average concentration of 10 mg/L); and during the wet period of 0 to 17 mg/L (average concentration of 6 mg/L). Data showed that nitrates were generally higher during the dry period, and at number of the sample locations exceeded the MCL (10 mg/L) during this period. Sample # 2 (La Crescenta), 3 (Eaton Canyon Falls), 4 (JPL), and 5 (Eaton Canyon Wash) showed low nitrate concentrations. These samples are located in the headwater areas, where there is no source for contamination. The samples with high nitrate levels were from the Sepulveda Basin area where the river flows down to Glendale and eventually to the ocean.

Nitrate sources in the watershed may be from wastewater treatment plant, garden and lawn fertilizers used in the region, street runoff, and nitrifying organisms. Nitrates are also high and above MCL at sample locations 6, 7, 8, 9, 10 and 11 where the river flows through highly populated regions of the city (Table 2). A comparison with LA River reference data (nitrate = 1 ppm) from Stein [13], shows that much higher nitrate concentration (mean value-ppm) for wet (5.91) and dry (10.12) periods were recorded for this study. This study showed slightly higher concentration values for nitrate, which are above MCL EPA drinking water standard (MCL=10 ppm) [23] (Table 4).

Phosphate analysis for the LA River showed a range of 0 to 1.65 mg/L during the dry period with an average concentration of 0.33 mg/L. For the wet season, the range was 0 to 0.67 mg/L and an average concentration of 0.14 mg/L (Table 2). The highest phosphate concentrations were recorded for the dry period (1.65 ppm) around Glendale Waste Water Treatment Plant where its effluent discharges to the LA River. Stein [13] showed phosphate concentration of 0.6 ppm in the LA River data. This study showed slightly lower phosphate concentrations for dry (mean=0.3 ppm, n=14) and slightly higher concentration for the wet period (mean=0.14; n=14) respectively (Table 4).

As secondary drinking standard parameter, sulfate may occur in water naturally and by anthropogenic sources [23]. The results of our water sampling and sulfate analysis showed that most samples are within the maximum contaminant levels (MCL) set by the USEPA except for areas known to have high levels such as sample 13 (PCH Bridge) and sample 14 (Queensway). Sulfate was also higher in sample 1 (Sepulveda Basin). The higher concentration level for this location may be due to the sulfate reaction that treatment plants used to neutralize the chlorine added to kill bacteria in the water treatment process. The dry period showed a range of concentrations for sulfate from 13 to 2,313 mg/L with an average concentration of 308 mg/L; and during wet periods, river concentrations of sulfate range from 7.9 to 746 mg/L with an average concentration of 121 mg/L. The US Environmental Protection Agency set sulfate MCL at 250 ppm [23] (Table 2).

3.3 Metals

As mentioned previously, the metals analyzed in this study include arsenic, lead, nickel, selenium, and zinc. The range of arsenic concentrations in this study was 1.3 to 4 ppb with an average concentration of 2.5 ppb for the dry period and 0.0016 to 0.016 ppb with an average

concentration of 0.0076 ppb for the wet period. Overall, Fig. 2 A shows a negative trend in the concentration of arsenic from the river headwaters to the ocean. An excess of these constituents can be harmful to human health. The US Environmental Protection Agency sets arsenic MCL at 10 ppb (0.010 mg/L) [23].

In the analysis of selenium, results showed a range of concentration from 0.2 to 3.0 ppb during the dry period and 0 to 0.009 ppb during the wet period. In the dry season selenium is lower in unlined locations 2 (La Crescenta), 3 (Eaton Canyon Falls), 4 (JPL) and 5 (Eaton Canyon Wash). Selenium may be removed from water and deposited in sediments. The higher selenium concentration was recorded in areas close to the GWWT recharge area and Rio Honda (Fig.2B). The US Environmental Protection Agency sets the MCL for selenium to be at 50 ppb (0.05 mg/L) [23] (Table 3).

Our analysis also showed that the nickel concentrations ranged from 0.9 to 10 ppb with an average of 4.4 ppb for the dry period and 0.0019 to 0.0085 ppb with an average concentration of 0.0045 ppb for the wet period. Except for the first sampling location (SB), all other sites showed a positive trend from the headwaters to the mouth of the river. The higher concentration

Table 2. Spatial and seasonal changes of various water parameter (anions) [ppm] for LA river

Sampling locations	Dist. km (mile)	Dry Season					Wet Season				
		Cl	F	NO ₃	PO ₄	SO ₄	Cl	F	NO ₃	PO ₄	SO ₄
1	71 (44.1)	101.7	0.6	16.8	0.0	151.9	122.4	0.7	17.1	0.0	361.4
2	63 (39.2)	5.7	0.2	1.2	0.0	35.6	5.9	0.1	1.6	0.0	30.1
3	58 (36.5)	9.2	0.9	1.0	0.0	13.3	4.7	0.6	0.7	0.0	8.9
4	58 (35.9)	12.6	1.0	1.8	0.0	24.4	3.4	0.4	5.7	0.0	12.1
5	56 (35.2)	5.5	1.0	0.0	0.0	14.9	4.2	0.5	1.6	0.0	8.0
6	47 (29.4)	97.4	0.6	21.5	1.7	118.0	30.6	0.4	7.2	0.4	70.8
7	40 (25.1)	106.7	0.6	16.7	0.7	123.3	22.7	0.3	6.0	0.3	69.1
8	40 (25.1)	82.5	0.3	18.9	0.0	119.0	14.4	0.3	5.9	0.0	21.9
9	40 (25.0)	93.9	0.5	18.4	0.4	120.5	66.1	0.5	11.2	0.0	125.0
10	35 (21.8)	103.4	0.6	16.5	0.6	124.0	16.7	0.4	5.9	0.0	34.7
11	26 (16.1)	101.7	0.6	16.8	0.0	151.9	25.1	0.3	6.6	0.3	72.3
12	6 (4.0)	108.2	0.6	6.5	0.6	146.6	20.0	0.3	6.6	0.2	67.8
13	5 (3.0)	5395.2	0.6	5.7	0.7	859.0	21.2	0.3	6.6	0.7	72.1
14	1 (0.9)	16027.4	0.0	0.0	0.0	2312.9	5860.4	0.0	0.0	0.0	746.0
MCL* (ppm)		250	4	10	na	250	250	4	10	na	250
Minimum (ppm)		5.51	0.00	0.00	0.00	13.31	3.39	0.00	0.00	0.00	7.98
Maximum (ppm)		16027.41	1.03	21.49	1.65	2312.94	5860.43	0.66	17.12	0.67	745.98
STD. Dev.		4391.44	0.29	8.40	0.48	613.97	1559.24	0.17	4.44	0.21	200.76
Average (ppm)		1589.36	0.56	10.12	0.33	308.24	444.14	0.37	5.91	0.14	121.43

The table also shows a comparison of average, standard deviation (SD), minimum, and the maximum of the various parameter in various locations in LA River. Sampling locations 1 and 14 were furthest and closest to the ocean. These locations including the Sepulveda Basin (1), La Crescenta (2), Eaton Canyon Falls (3), JPL Area (4), Eaton Canyon Wash (5), Glendale Narrows (6), Under the bridge near Confluence (7), Lower Arroyo Seco (8), Arroyo Seco Confluence (9), First and Seventh Street (10), City of Bell (11), Willow Street in Long Beach (12), Pacific Coast Highway Bridge (13) and Queensway in Long Beach (14) (The Mouth of the LA River). MCL=Maximum Contamination Limit, na = not available. . *(after [23]). N (dry)=14 and N (wet)=14

Table 3. Dry and wet period concentration changes (ppb) of various metals for Los Angeles river

Sampling Location	Dist km (miles)	Dry Season					Wet Season				
		Ni	Zn	As	Pb	Se	Ni	Zn	As	Pb	Se
1	71 (44.1)	6.89	62.41	3.03	1.05	3.03	0.01	0.04	0.01	0.00	0.00
2	63 (39.2)	0.94	1.05	2.88	0.02	0.70	na	na	na	na	na
3	58 (36.5)	1.10	2.06	3.88	0.05	0.25	na	na	na	na	na
4	58 (35.9)	1.25	0.85	2.91	0.01	0.22	0.00	0.00	0.01	0.00	0.01
5	56 (35.2)	1.10	6.10	1.44	0.23	0.20	0.00	0.00	0.02	0.01	0.01
6	47 (29.4)	4.85	30.33	2.24	0.28	2.58	0.01	0.02	0.01	0.00	0.00
7	40 (25.1)	5.32	25.03	2.50	0.27	2.52	0.00	0.00	0.00	0.00	0.00
8	40 (25.1)	2.86	3.31	1.38	0.04	1.30	0.00	0.02	0.01	0.00	0.00
9	40 (25.0)	3.15	4.85	1.63	0.08	1.46	0.00	0.02	0.01	0.00	0.01
10	35 (21.8)	4.88	21.85	2.85	0.25	2.30	0.00	0.01	0.00	0.00	0.00
11	26 (16.1)	6.19	40.95	2.70	0.51	2.31	0.00	0.02	0.02	0.00	0.00
12	6 (4.0)	6.01	39.21	2.55	0.48	2.21	0.01	0.01	0.00	0.00	0.00
13	5 (3.0)	6.48	27.80	16.88	0.47	28.15	0.00	0.01	0.00	0.00	0.00
14	1 (0.9)	10.25	21.31	75.60	0.27	170.43	0.00	0.00	0.00	0.00	0.00
MCL (ppb)*		100	5000	10	15	50	100	5000	10	15	50
Minimum (ppb)		0.94	0.850	1.377	0.009	0.198	0.002	0.000	0.002	0.001	0.000
Maximum (ppb)		10.25	62.414	3.880	1.054	3.027	0.009	0.039	0.017	0.006	0.009
STD. Dev.		2.77	18.710	0.730	0.281	1.036	0.002	0.011	0.005	0.002	0.003
Average (ppb)		4.38	20.508	2.499	0.287	1.589	0.005	0.013	0.008	0.003	0.003

The table also shows a comparison of average, standard deviation (SD), minimum, and the maximum of the various parameter in different locations in LA River. Sampling location 1 and 14 were furthest and closest to the ocean. These locations including the Sepulveda Basin (1), La Crescenta (2), Eaton Canyon Falls (3), JPL Area (4), Eaton Canyon Wash (5), Glendale Narrows (6), Under the bridge near Confluence (7), Lower Arroyo Seco (8), Arroyo Seco Confluence (9), First and Seventh Street (10), City Bell (11), Willow Street in Long Beach (12), Pacific Coast Highway Bridge (13) and Queensway in Long Beach (14) (The Mouth of the LA River). MCL=Maximum Contamination Limit, na = not available. *(all after [23]USEPA, 2012 except nickel, which is after Title 22 of the California Code of Regulations). N (dry)=14 and N (wet)=14

was recorded in areas close to the Glendale WWTP recharge area and Rio Honda. The highest concentration was at Queensway in Long Beach (site 14) (Fig. 2C). According to Title 22 of the California Code of Regulations the MCL for nickel is 100 ppb (0.1 mg/L) [23] (Table 3).

Lead showed a concentration range from 0.008 to 1.05 ppb (average concentration of 0.29 ppb) for the dry period and 0.00099 to 0.0058 ppb (average concentration of 0.0029 ppb) for the wet period. Although the concentration values for lead is below MCL. Sampling location 1 (SB) showed the highest values. Glendale Narrows, City of Bell, and the southern part of Los Angeles showed high values probably because of solid waste disposal (Table 3) (Fig. 2D). The US Environmental Protection Agency has set the lead MCL to be at 15 ppb (0.015 mg/L) [23].

Analytical results showed the range of concentration for zinc to be 0.8 to 63 ppb with an average concentration of 20.5 ppb during the dry period and 0 to 0.038 ppb and an average of 0.012 ppb for the wet period. The higher concentrations were recorded in areas close to the Tillman WWTP recharge area and the Rio Honda site (Fig. 2E). Overall, the results showed low concentration for zinc which did not exceed

the MCL (Table 3). According to USEPA [23], zinc MCL is set at 5,000 ppb (5 mg/L) level.

4. DISCUSSION

The California Regional Water Quality Control Board has set the pH standard for inland waters to be at a range of 6.5 to 8.5 [19]. The LA River showed pH values within the specified range for both seasons except for one location, PCH (sample 13), which had a pH of 4.88 during the dry period. Traces of solid waste (non-point source pollution) were evident in most sampling locations, which is the most likely cause of the pH change during the dry period. Dumping industrial pollutants directly into the river water can affect its pH. Groundwater has little effect on the pH of the entire river system since the majority of the water volume (72% according to Ackerman et al., flowing in the LA River during dry period was mostly discharged from the wastewater treatment plants [10,24].

Dissolved oxygen and salinity are additional parameters that are used to determine the physio-chemical characteristics of water in the LA River watershed. To support aquatic life, a threshold dissolved oxygen level is needed. Low dissolved oxygen levels result in the anaerobic

condition that can cause fish kills and create odors. The California Regional Water Quality Control Board specifies that the mean annual dissolved concentrations of oxygen in all waters shall be greater than 7 mg/L and no single sampling shall be less than 5 mg/L, except when natural conditions cause lesser concentrations [19]. Results in this study have shown that DO values are within levels needed to support aquatic life.

As for salinity, this parameter in the LA River watershed is locality dependent. Salinity originates from the river-ocean interaction at the mouth of the river and also from the treatment process at the Tillman wastewater reclamation plant, where the effluent discharge point is located. Consequently, the higher salinity values income from samples in the Sepulveda Basin sample, next to the Tillman wastewater treatment plant, as well as from samples closer to the ocean in Long Beach area. The wastewater treatment plant (WWTP) uses sodium hypochlorite (NaOCl) to disinfect water after tertiary treatment and which later on is dechlorinated by using sodium bisulfite (NaHSO₃). The chemical reaction will produce salt (NaCl):

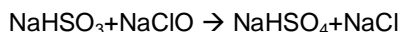


Table 4. Comparison of the average concentrations (nickel, lead, and zinc) found in this study with concentrations found in other water bodies and with international water quality guidelines

Sites	Ni (ppb)	Pb (ppb)	Zn (ppb)
This study (2012) (N (dry)=14)	4.38	0.287	20.50
Taipu River, China [25]	15.00	57	98
Hindon River, India [26]	na	276	110
Yangtze River, China [27]	13.00	55	9
Los Angeles River [13]	3.00	2	122
Los Angeles River [22]	11.24	29.9	127
San Gabriel River [13]	9.00	3	213
San Jose Creek [13]	5.00	2	117
Walnut Creek, CA, USA [13]	1.00	3	73
Ballona Creek, CA, USA [13]	5.00	4	79
WHO [28]	100*	10	3000
US EPA Standard [23]	na	15	5000

*After Title 22 of the California Code of Regulations; na=not available

The correlation coefficient between chloride and sulfate is $r = 0.99$ (Table 6). This strong

correlation indicates that the chemical reaction between sodium hypochlorite and sodium bisulfate confirms the salt byproduct and explains the higher salinity values near the treatment plant.

Salinity concentration also increases where the river meets the ocean. During high tide, ocean water flows upstream, where ocean water mixes with fresh water. The inflow of ocean water is visible at the PCH Bridge (Sampling location 8).

Several anions were analyzed in this research including primary and secondary drinking water contaminants. Chloride and sulfate are listed as the national secondary drinking water standard contaminants. Fluoride (MCLG=4 mg/l) is now included in both the primary and secondary drinking water standard. Most fluoride compounds have low solubility; hence, fluoride occurs only in small amounts in natural waters. Too much fluoride can cause bone disease and mottled teeth in children [23].

Table 5. Dry-wet correlation coefficient for various anions and metals for LA River water

Parameter/ contents	Wet and Dry-correlation	T-Test p-value
Cl	0.95	0.09
F	0.74	0.00
NO ₃	0.67	0.01
PO ₄	0.62	0.05
SO ₄	0.86	0.07
Ni (ppb)	0.33	0.00
Zn(ppb)	0.67	0.00
As(ppb)	-0.30	0.07
Pb(ppb)	0.14	0.00
Se(ppb)	-0.35	0.11
Dissolved Oxygen (DO)	-0.04	0.06
pH	-0.02	0.01
Temp (°C)	0.55	0.00
Salinity	0.93	0.11

Nitrate is another nutrient that can originate from natural deposits and also from human activity. Most of the time in the Los Angeles region nitrate originates from runoff and from garden fertilizer, septic tanks, and sewage [29]. The excess amount of nitrate will cause illness such as shortness of breath and “blue baby syndrome” [30]. Excessive nitrate levels can also lead to excess aquatic plant growth that can then also contribute to the increased levels of nitrates [23]. Nitrate interferes with chlorine disinfection; depletes oxygen levels in receiving waters, stimulates algae growth, and promotes eutrophication that may increase the toxicity of water due to ammonia.

Phosphate is a nutrient that may not be highly toxic to humans and animals, but it may cause digestion problems at a very large concentration [23]. Comparing the data from Ackerman et al, (2000) with this work, it is clear that sulfate and chloride are highest in the area close to the Tillman Wastewater Reclamation Plant.

Lead can be added to the aquatic system by natural erosion of rocks. Other sources for lead is solid waste trash in river such as building materials and pipes [30]. Comparison of wet vs. dry weather loading indicates that dry weather loading can be a significant source of metals, ranging from 0.02 to 0.01 ppb and during wet years from 1.3 to 3.8 ppb during dry years. Our results show increasing concentrations of lead towards the ocean in the dry period except for sample 1 (SB). Formation of lead salts can be caused by high sulfate and carbonate concentrations in water. Higher amounts of sulfate in the Sepulveda Basin and Queensway may result in higher lead concentrations. According Polanskiy [31] water in the presence of oxygen attacks lead to start an accelerating reaction. The presence of carbonates or sulfates results in the formation of insoluble lead salts.

Selenium sources can be natural or unnatural, such as discharge from various industrial sites. Excess selenium can cause hair or fingernail loss, numbness of fingers and problems in the circulatory system [23]. Results for selenium during the dry period show that there is a low concentration at natural and unlined areas of the watershed including La Crescenta (2), Eaton Canyon Falls (3), JPL (4) and Eaton Canyon Wash (5). Selenium cannot be easily dissolved in water and is mostly deposited in sediments. Suspended solid particles in water can also harbor trace metals. Under oxidizing conditions, arsenic and selenium exist in solution as negatively charged species. These species are adsorbed at low pH when particle surfaces are positively charged. Under strongly oxidizing conditions arsenic occurs as the arsenate (+5) species, which forms inner-sphere complexes and is strongly adsorbed by iron oxyhydroxides. Under the same conditions, selenium occurs as the selenate (+6) species which is only weakly adsorbed. Under less oxidizing conditions, the situation is reversed with the less oxidized arsenite (+3) species only weakly adsorbed at all pH values while the selenite (+4) species is strongly adsorbed. According to Lu et al. [32], during atmospheric deposition of metal-bearing particles, large particles dominate local trace

metal deposition in central urban and adjacent area in LA basin. These particulates can become trapped within soil matrices [32] and then enters by runoff to rivers aquatic system. This study showed that the arsenic, lead, selenium, and nickel values are very low in concentrations and are also below the MCL set by EPA for each target metal. Sediment analysis could be a useful tool to better understand the river watershed hydrochemistry in this region. In the LA River basin, the sources for the metals are natural and anthropogenic. If these metals were to increase in concentration, the health and environment is at risk. Too much arsenic, lead, nickel, selenium, and zinc are toxic and may be fatal to humans. Aquatic life may also be affected in elevated levels of metals in surface waters. Slightly elevated metal levels in natural water may cause morphological changes in tissues, suppression of growth, and change in enzyme activity and reproduction in the aquatic organism [33].

The two major factors that control the mobility of the transition metals, zinc, cadmium, and lead in the natural environment, first oxidation-reduction conditions and second pH. In the natural environment, most of these metals exist as divalent or trivalent cations. At high pH many of these elements form insoluble oxyhydroxides and/or carbonates. Also, adsorption becomes an important process with increasing pH and these metals are removed by adsorption to particles.

Comparing of the mean concentrations level (n=14) of nickel from this research study with other rivers showed that our values for LA River are less than those reported by SWQCB [19] and much lower than the concentration levels of nickel reported in Taipu [25] and Yangtze River [27], in China. The concentration of nickel is overall lower than MCL (100 ppb). We have also compared the nickel concentration in our study area with nickel concentrations reported in Stein and Ackerman's paper data [13] for the San Gabriel River, San Jose River, LA River, Walnut, and Ballona Creeks, in California. Our results are very close to those listed for the LA River water by Stein and Ackerman [13]. The nickel concentrations (ppb) rank from highest to lowest is LA River 11.24 (ppb) [22]>San Gabriel River, 9 [13] > San Jose Creek, 5 [13] > Ballona Creek, 5 [13] > LA River, this study, 4.38 > LA River, 3 [13] > Walnut Creek, 1ppb [13] (Table 4). The Ballona Creek, San Jose Creek, and other watershed were selected for this analysis because they are representative of highly urbanized watersheds in southern California.

Table 6. The table shows the correlation between pairs of parameter with dry weather condition data set

	Dist	Cl	F	NO3	PO4	SO4	Ni	Zn	As	Pb	Se	DO	pH	Temp	Salinity
Dist	1														
Cl	-0.62	1.00													
F	0.37	-0.52	1.00												
NO3	0.06	-0.38	-0.17	1.00											
PO4	-0.65	0.67	0.03	-0.39	1.00										
SO4	-0.65	0.99	-0.55	-0.32	0.07	1.00									
Ni	-0.69	0.67	-0.49	0.22	0.21	0.72	1.00								
Zn	-0.23	0.05	-0.09	0.41	0.11	0.11	0.72	1.00							
As	-0.56	0.99	-0.53	-0.39	-0.16	0.99	0.65	0.04	1.00						
Pb	-0.10	0.05	0.00	0.27	0.07	0.10	0.62	0.95	0.03	1.00					
Se	-0.56	0.99	-0.55	-0.36	-0.15	0.98	0.66	0.05	0.99	0.03	1.00				
DO	0.03	-0.62	0.29	0.01	-0.26	-0.62	-0.39	-0.02	-0.62	-0.04	-0.62	1.00			
pH	0.17	-0.03	-0.18	-0.20	-0.43	-0.04	-0.01	0.11	0.08	0.08	0.10	0.37	1.00		
Temp	-0.26	0.05	-0.14	0.62	0.23	0.11	0.73	0.90	0.04	0.81	0.06	-0.02	0.04	1.00	
Salinity	-0.59	0.99	-0.53	-0.35	-0.17	0.99	0.71	0.13	0.99	0.13	0.99	-0.60	0.03	0.13	1.00

Our result for mean lead concentration (ppb) showed much lower levels for the LA River compared to other rivers. The lead concentration (ppb) rankings is LA River, 29.9 [22], 2005> Ballona Creek, 4 [13] > San Gabriel River, 3 [13] and Walnut Creek, 3 [13] > San Jose Creek, 2 [13] > LA River 2 [13] > this study, 0.28 ppb (Table 4).

Comparing our results (mean value) for zinc (n=14) with other rivers concentration (ppb) value reveals that the San Gabriel River had the highest (213 ppb) and our study area showed the lowest (20.50 ppb). A concentration rank shows that San Gabriel River, 213 [13]> LA River, 127 [22] > LA River, 122 [13] > San Jose Creek, 117 [13] > Creek, 79 [13]> Walnut Creek, 73 [13] > this study, 20.50 ppb (Table 4).

The statistical analysis values show some discrepancy in dry and wet season values for a few parameters. Correlation coefficients and p-values were calculated for the parameters tested in this study for 2 groups of data in wet and dry periods. Correlation coefficient values are shown in Table 5 with negative values for arsenic, selenium, DO, and pH. Nitrate, fluoride, phosphate, nickel, zinc, lead, pH and temperature showed statistically significant values in the dry and wet season (p-value < 0.05). Chloride, sulfate, arsenic, selenium, DO, and salinity showed a p-value (0.05<p-value< 0.10) indicating that are not significant statistically (high-moderate). Fig. 2F shows the correlation of some of the physio-chemical parameters in the wet and dry season.

As a general rule, correlation coefficient (r) tells us how much one variable tends to change when the other one does. Correlation coefficient (r) with absolute values that are, the distance from zero, of 0.3 or less are considered to be weak, 0.3 to 0.7 are considered moderate, and 0.7 or higher are considered strong. The results of the statistical analysis show a correlation coefficient of 0.95 for chloride. This means that there's a very strong correlation between the chloride concentration of samples in dry and wet weather periods. Determining whether two sets of values are correlated is in one sense, a mathematical question, but a correlation coefficient of 0.95 does not mean that some invisible factor makes two unrelated data sets change at the same rate.

The dry weather conditions showed overall higher concentrations in most of the measured

parameters. A correlation between these parameters reveals the relationship between the pairs of data in one group (Table 6). The (chloride-sulfate), (chloride-arsenic), (chloride-selenium), (chloride-salinity), (arsenic-selenium), (arsenic-salinity), and (zinc-lead) showed a correlation coefficient of r=0.99.

The constituent loads for stream sites were calculated by multiplying flow and concentrations for each sample (Eq. 1):

$$\text{Load} = \sum F_i C_i \quad (\text{Eq. 1})$$

Where F_i was the flow at sampling location averaged over the period and C_i was the constituent concentration at locations i resulting from sampling.

In using the average monthly discharge of the LA River from the water data of the USGS, we can calculate the Sulfate and Nitrate loads on the river in kg/day (or tons/day). From 1930 to 1992 the average discharge for February and July are 698 cfs and 36 cfs [34].

Sulfate in the river has an average concentration of 308 mg/L during the dry period and 121mg/L during the wet period. The calculated load is 29,900 kg/day (29.9 t/day) and 228,000 kg/day (228 t/day) during the dry and wet periods, respectively. Nitrate has an average concentration of 10 mg/L during the dry period and 5.9 mg/L during the wet period. Values from these calculations show a total nitrate load of 980 kg/day (0.97 t/day) and 11,100 kg/day (11.1 t/day) during the dry and wet period, respectively. Comparing the above values for nitrate with Stein and Ackerman's study [13], our study shows lower pollutant loading. Nitrate loading recorded by Stein and Ackerman's study [13] shows 363 kg/day and 2,529.5 kg/day for the year 2000 and 2001, respectively. Furthermore, the latter study shows that the source of nitrate loading is attributed to storm drains (63% for the year 2000; 31% for the year 2001) and WWTPs (69% for the year 2001). Estimates of dry weather loading are naturally variable; therefore, repeated time-series measurement will be necessary in order to clear the uncertainty associated with these estimates.

5. CONCLUSION

This research study shows that the LA River's physical and chemical parameters are not at natural water levels for most sample locations for dry weather runoff. The majority of the water

flowing in the river comes from treated water from the Tillman, Burbank, and Glendale wastewater treatment plant and some from groundwater discharge. The anions trend results show that the river has higher concentrations during the dry period than the wet period and that this difference is perhaps due to the water flow differences between the two periods. The river has anion concentrations at levels below the MCL except for areas affected by salinity input such as the mouth of the LA River, which also affects chloride and sulfate concentration values. As for nitrates, concentration levels are above the MCL during the dry period. The levels are believed to result from agricultural runoff along Sepulveda Basin and street runoff along the highly dense industrial and residential area of the Los Angeles.

The metal analysis was done for both wet and dry periods of the river. Results show very low concentrations for the metals of interest. Trends show that dry period samples have higher concentrations compared to wet period concentrations. Further monitoring of chemical inputs for "urban water" can help identify the sources of contamination. While this study showed that the concentration values of most metals were lower than MCL, it also suggests the city should enforce regulation for urban runoff, street and industrial runoff, point and nonpoint source pollutants, and dumping of waste along the river. The study of sediments (in the unlined section of river) and organic substances in water was not performed in this research study. It would be helpful to know what contaminants have leached into the ground and how this could affect the watershed and water chemistry. Further future work would involve the use of stable isotope signatures of the river water to understand the watershed dynamic. The Los Angeles City and some other non-profit organizations groups such as the Friends of the Los Angeles River (FOLAR) have undertaken efforts to revitalize the river. Volunteers from around the city are trying to clean up the river and make it a place for recreation. The LA River Master Plan aims at environmental enhancement, recreational activities and economic development for the river. So far, parts of the river have developed landscapes for recreation and it was just recently opened for kayak enthusiasts. A future with sustainable cities requires initiatives that grow from the nexus of social, economic, cultural, and environmental research and policy development and implementation.

ACKNOWLEDGEMENTS

We would like to thank Dr. Baron, CSU Bakersfield, Geology Department, Drs Dehyen-Latz Laboratory at Scripps Institute of Oceanography at UCSD, who generously helped us with the ICP MS analysis at their laboratories; Dr. Ellis for using the Hydrogeology Laboratory at CSULA, where we analyzed all the anions using Ion Chromatography. Special thanks to Matthew Luque for helping out with the water sampling and analysis used in this study. And last but not least, we would like to thank Drs Bishop and Ellis for reviewing this work as part of the graduate thesis of Carl Von Co.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Lin KC, Lee YL, Chen CY. Metal toxicity to *Chlorella pyrenoidosa* assessed by a short-term continuous test. *J. Hazard. Mater.* 2007;142:236–241. [PubMed]
2. Sabin L, Lim J, Stolzenback K, Schiff K. Atmospheric dry deposition of trace metals in the coastal region of Los Angeles CA, USA. *Environmental Toxicology and Chemistry/SETAC.* 2006;25:2334.
3. Moon S, Huh Y, Zaitsev A. Hydrochemistry of the Amur River: Weathering in a northern temperate basin. *Aquatic Geochemistry.* 2009;15(4):497-527.
4. White AF, Blum AE. Effects of climate on chemical weathering in watersheds. *Geochimica et Cosmochimica Acta.* 1995; 59(9):1729–1747.
5. Kumar RN, Solanki R, Kumar JIN. Seasonal variation in heavy metal contamination in water and sediments of river Sabarmati and Kharicut canal at Ahmedabad, Gujarat. *Environ. Monit. Assess.* 2013;185:359–368. DOI: 10.1007/s10661-012-2558-4. [PubMed]
6. Rezaie-Boroon MH, Gnandi K, Tomety Folly K. Presence and distribution of toxic trace elements in water and sediments of the southern Togo rivers watershed, West Africa. *PSP, Environmental Bulletin.* 2011; 20(7).
7. Los Angeles County Department of Public Works; 2010.

- Available:<http://dpw.lacounty.gov/wmd/watershed/la>
8. Tetra Tech Inc. Los Angeles County Watershed Model Configuration and Calibration- Part II-Water Quality. Submitted to County of Los Angeles; 2010.
 9. Varnelis K. The infrastructural city: Networked ecologies in Los Angeles., Actar, The Network Architecture Lab Columbia University and The Los Angeles Forum for Architecture and Urban Planning; 2008.
 10. Ackerman D, Schiff K, Trim H, Mullin M. Characterization of water quality in the Los Angeles river. Bulletin of the Southern California Academy of Sciences. 2003; 102(1).
Available:<http://scholar.oxy.edu/scas/vol102/iss1/3>
 11. Schiff K, Allen MJ, Zeng EY, Bay SM, Southern CA. Marine Pollution Bulletin. 2000;41(1-6):76-93.
 12. Sunny J. Is urban runoff a source of human pathogenic viruses to recreational beach waters? Technical Completion Report W-943; 2004, University of CA, Irvin. Bilodeau WL, Bilodeau SL, Gath EM, Osborne M, Proctor RJ. Geology of Los Angeles, California, United States of America. Environmental & Engineering Geosciences. 2007;13(2):99-160.
 13. Stein E, Ackerman D. Dry-Weather water quality loadings in arid, urban watersheds of the Los Angeles basin, California, USA. JAWRA Journal of the American Water Resources Association. 2007;43(2):398-413.
 14. Gallo EL, Lohse KA, Brooks PD, McIntosh JC, Meixner T, McLain JET. Quantifying the effects of stream channels on storm water quality in a semi-arid urban environment. Journal of Hydrology. 2012; 470-471,98-110.
 15. Stein E, Ackerman D, Schiff K. Watershed-based sources of contaminants to San Pedro Bay and Marina del Rey: Patterns and trends', Southern California Coastal Water Research Project Technical Report #413, Westminster, CA. 2003;31.
 16. Schueler TR. The importance of imperviousness', in Schueler TR, Holland HK. (eds.) The Practice of Watershed Protection, Watershed Protection Techniques, Ellicott City, MD: Center for Watershed Protection. 2000;100-111.
 17. State Water Control Board (SWRCB), California Environmental Protection Agency; 2008.
Available:http://www.swrcb.ca.gov/water_issues/programs/tmdl/303d_lists.shtml
 18. Stein ED, Tiefenthaler LL. Dry weather metals and bacteria loading in an arid urban watershed: Ballona Creek, CA. Water, Air, and Soil Pollution. 2005;164: 367-382.
 19. State Water Quality Control Plan Los Angeles Region Review sheet (SWQCB); 1994.
Available:http://www.waterboards.ca.gov/losangeles/water_issues/programs/basin_plan/
 20. Tetra Tech, Inc. Modeling Analysis for Development of TMDLs for Metals in the LA River and Tributaries. Los Angeles Regional Water Quality Control Board, USEPA-Region 9; 2004.
 21. US Environmental Protection Agency (USEPA) National Primary Drinking Water Standards Contaminants. Retrieved August 24; 2007.
Available:www.epa.gov/safewater/contaminants/index.html
 22. California Department of Water Quality Control Board, Final Report; 2005.
Available:http://www.waterboards.ca.gov/water_issues/programs/tmdl/records/region4/2009/ref3246.pdf
 23. U.S. Environmental Protection Agency (USEPA) Edition of the Drinking Water Standards and Health Advisories. Office of Water, U.S. Environmental Protection Agency; Washington, DC, USA: 2012. EPA 822-S-12-001.
 24. Trim H. Beneficial uses of the Los Angeles and San Gabriel rivers. Los Angeles, Calif.: Los Angeles and San Gabriel Rivers Watershed Council; 2001.
 25. Yao H, Qian X, Gao H, Wang Y, Xia B. International Journal Environmental Research Public Health. 2014;11(11). PMC4245648.
 26. Suthar S, Nema AK, Chabukdhara M, Gupta SK. Assessment of metals in water and sediments of Hindon river, India: Impact of industrial and urban discharges. J. Hazard. Mater. 2009;171:1088-1095. DOI:10.1016/j.jhazmat.2009.06.109.[PubMed] [Cross Ref]
 27. Wu B, Zhao DY, Jia HY, Zhang Y, Zhang XX, Cheng SP. Preliminary risk assessment of trace metal pollution in

- surface water from Yangtze river in Nanjing section, China. Bull. Environ. Contam. Toxicol. 2009;82:405–409.
DOI: 10.1007/s00128-008-9497-3. [PubMed] [Cross Ref]
28. World Health Organization (WHO), Guidelines for Drinking Water Quality Recommendations Incorporating 1st and 2nd Addenda. 13th ed. 2008 WHO; Geneva, Switzerland.
 29. California Department of Public Health (CDPH); 2010.
Available:<http://www.cdph.ca.gov/certlic/drinkingwater/Pages/Nitrate.aspx>
 30. Fetter CW. Contaminant hydrogeology, Prentice Hall. 2007;500.
 31. Polanskiy. Analytical Chemistry of the Elements: Lead] (in Russian); 1985. in Wikipedia.com
 32. Lu R, Turco RP. Stolzenbach K, Friedlander SK, Xiong C, Schiff KC, Tiefenthaler L, Wang G. Dry deposition of airborne trace metals on the Los Angeles Basin and adjacent coastal waters. Santa Monica Bay Restoration Project, Los Angeles, CA, Southern California Coastal Water Research Project, Westminster, CA, Institute of the Environment, University of California, Los Angeles, CA. Journal of Geophysical Research. 2003;108(D2): 4074.
 33. Osmond DL, Line DE, Gale JA, Gannon RW, Knott CB, Bartenhagen KA, Turner MH, Coffey SW, Spooner J, Wells J, Walker JC, Hargrove LL, Foster MA, Robillard PD, Lehning DW. WATERSHEDSS: Water, Soil, and Hydro-Environmental Decision Support System; 1995.
 34. USGS, US Geological Survey; 2012.
Available:<http://waterdata.usgs.gov/ca/nwis/monthly>

© 2015 Boroon and Co; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:
The peer review history for this paper can be accessed here:
<http://sciencedomain.org/review-history/11479>